

DESCRIPTION

LIQUID ABSORBING SHEET AND
NONAQUEOUS ELECTROLYTE BATTERY PACK

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TECHNICAL FIELD

The present invention relates to a liquid absorbing sheet for absorbing an electrolyte solution when such a solution leaks from a nonaqueous electrolyte battery cell encased in a nonaqueous electrolyte battery pack. The present invention also relates to a nonaqueous electrolyte battery pack that uses such a liquid absorbing sheet.

15 BACKGROUND ART

Battery packs are widely used that have a plurality of primary or secondary battery cells, a circuit board, and a battery case encasing these components. When an electrolyte solution leaks from any of the battery cells, it can corrode the wiring of the circuit board, resulting in a conduction failure or short circuit. To prevent such corrosion and short circuits when leakage of the electrolyte solution occurs, a liquid absorbing element containing an absorbent capable of absorbing the electrolyte solution is arranged in the battery pack adjacent to

or in the vicinity of the battery cell (Japanese Patent Application Laid-Open No. 2001-351588).

Various polymer materials are used as the absorbent, including adsorbents, gelling agents and self-swelling agents. Among specific examples of the absorbents described are polyacrylate-based water-absorbing resins, starch/graft copolymer-based water-absorbing resins, polyvinyl alcohol-based water-absorbing resins, polyacrylamide-based water-absorbing resins, isobutylene-maleic acid copolymer-based water-absorbing resins, long chain alkyl acrylate crosslinked polymers, and polynorbornens.

One drawback of these absorbents is that they cannot effectively absorb propylene carbonate, dimethyl carbonate and other carbonate-based solvents that are widely used in nonaqueous electrolyte battery packs, a type of batteries that have become increasingly used in recent years. Specifically, these solvents are used in nonaqueous electrolyte secondary cells that make lithium ion-based nonaqueous electrolyte secondary battery packs.

The present invention addresses the above-described problem and to that end, it is an objective of the present invention to provide a liquid absorbing sheet capable of effectively absorbing the nonaqueous electrolyte solution used in nonaqueous electrolyte

secondary cells that make nonaqueous electrolyte battery packs (in particular, lithium ion-based nonaqueous secondary battery packs). It is another objective of the present invention to provide a
5 battery pack equipped with an electrolyte-absorbing element made of such a liquid absorbing sheet.

DISCLOSURE OF THE INVENTION

In the course of our study, the present inventors
10 have found that a resin layer obtained in a particular manner can absorb and retain significant amounts of an electrolyte solution, the finding leading to the present invention. Specifically, this resin layer is obtained by irradiating UV-rays onto a particular
15 monomer composition to polymerize the composition and thereby make a sheet. This monomer composition contains the following components: a monofunctional monomer component (A) comprising a monofunctional monomer (a) capable of forming a homopolymer that is
20 soluble in nonaqueous solvents used in nonaqueous electrolyte secondary batteries; and a polyfunctional monomer component (B).

Specifically, the present invention provides a liquid absorbing sheet comprising a liquid-absorbing
25 resin layer, wherein the liquid-absorbing resin layer is obtained by irradiating UV-rays onto a monomer

composition to polymerize the monomer composition, the monomer composition containing:

a monofunctional monomer component (A) containing a monofunctional monomer (a) capable of forming a homopolymer that is soluble in a nonaqueous solvent used in a nonaqueous electrolyte secondary battery; and

a polyfunctional monomer component (B).

The present invention also provides a nonaqueous electrolyte battery pack having a nonaqueous electrolyte battery cell, a circuit board, an electrolyte-absorbing element for absorbing an electrolyte solution in the event of electrolyte leakage from the nonaqueous electrolyte battery cell, and a battery case encasing all of the above components, wherein the electrolyte-absorbing element is formed of the above-described liquid absorbing sheet.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A, 1B, and 1C are each a cross-sectional view showing a liquid absorbing sheet of the present invention.

Fig. 2 is a perspective view showing a nonaqueous electrolyte battery pack of the present invention.

Fig. 3 is a perspective view showing another

nonaqueous electrolyte battery pack of the present invention.

Fig. 4 is a diagram illustrating an electrolyte absorption test conducted using a model battery pack.

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BEST MODE FOR CARRYING OUT THE INVENTION

First the liquid absorbing sheet of the present invention will be described below in more detail.

The liquid absorbing sheet of the present invention can be provided in different forms. For example, the liquid absorbing sheet may be provided as an independent sheet formed entirely of a liquid absorbing resin layer 1 (Fig. 1A), or it may comprise a substrate 2 with the liquid absorbing resin layer 1 formed on one side (Fig. 1B). Alternatively, the liquid absorbing sheet may include an adhesive layer 3 formed over the liquid absorbing resin layer 1 (Fig. 1C). The liquid absorbing sheet with the configuration shown in Fig. 1C can be easily secured in a battery case. The adhesive layer 3 may be formed of any conventional adhesive. The liquid absorbing sheet of the present invention may not include the substrate: it may be the adhesive layer formed on one side of the liquid absorbing resin layer (the configuration shown in Fig. 1C without the substrate 2).

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While the adhesive layer 3 may be formed of any conventional adhesive, it is preferably formed of a liquid absorbing resin layer that itself shows adhesion. Whether a liquid absorbing resin exhibits adhesion or not depends on its composition, as will described later. By using the adhesive layer 3 that serves both as an adhesive and as a liquid absorber, the amount of the liquid that the liquid absorbing sheet can absorb can be increased as compared to a liquid absorbing sheet using a simple adhesive layer that does not absorb a liquid. We will describe this later in the description.

Although the substrate 2 for use in the liquid absorbing sheet of the present invention may be a resin film that is impermeable to electrolyte solutions (such as a plastic film made of polypropylene or other materials), it may be a material that can absorb and retain the nonaqueous solvent, including nonwoven fabric or synthetic paper formed of plastic fibers such as polypropylene, or paper. The substrate made of such a nonwoven fabric can absorb the nonaqueous solvent at an increased rate.

The liquid absorbing resin layer 1 to form the liquid absorbing sheet of the present invention may be a polymer film obtained by irradiating UV-rays onto a particular monomer composition to polymerize the

composition and thereby make a sheet. This monomer composition contains the following components: a film-forming, monofunctional monomer component (A) comprising a monofunctional monomer (a) capable of forming a homopolymer that is soluble in nonaqueous solvents used in nonaqueous electrolyte secondary batteries; and a crosslinkable, polyfunctional monomer component (B).

The monofunctional monomer component (A) for use in the present invention must be a monofunctional monomer (a) that can form a homopolymer soluble in nonaqueous solvents used in nonaqueous electrolyte secondary batteries. This is because, if the monofunctional monomer component (A) is composed solely of a monofunctional monomer that forms a homopolymer insoluble in such nonaqueous solvents, the ability of the resulting resin layer to absorb the nonaqueous solvent becomes insufficient. By saying "a homopolymer is soluble in a nonaqueous solvent," it is meant that the weight of the homopolymer is decreased by at least 10% when 1 part by weight of the homopolymer is immersed in 30 parts by weight of a nonaqueous solvent for 24 hours at room temperature (approx. 23°C). The nonaqueous solvent is especially, a mixed solvent containing at least one of dimethyl carbonate, propylene carbonate, and ethylene carbonate,

which will be described later in the description. The mixture preferably contains equal volumes of the respective solvents. The decrease in weight can be determined by comparing the dry weight of the

5 homopolymer measured after the homopolymer has been immersed in the nonaqueous solvent and then pulled out of the solvent, with the weight measured prior to the immersion period. A 100% decrease in weight means that the homopolymer has been completely dissolved in

10 the solvent.

The monofunctional monomer (a) is such that the difference in the solubility parameter value (*i.e.*, SP value $(J/cm^3)^{1/2}$) between the monofunctional monomer and a given nonaqueous solvent used in a nonaqueous

15 electrolyte secondary battery to which to apply the liquid absorbing sheet preferably falls within the range of -1.0 to 8.0 and, more preferably, within the range of 2.0 to 6.5. If this difference falls outside the specified range, the homopolymer becomes

20 substantially insoluble in the nonaqueous solvent, resulting in an insufficient ability of the resulting resin layer to absorb the solvent.

The solubility parameter is determined by the Fedors equation shown below (See, R.F.Fedors, Polym. Eng. Sci., 14(2), p147, p472 (1947)). The solubility

25 of the monofunctional monomer in the present invention

was determined for polymerized repeating units. In the following Fedors equation, ' σ ' indicates the solubility parameter, ' V ' indicates the molar volume (cm^3/mol) and ' E_{coh} ' indicates the binding energy (J/mol):

$$\sigma = (\Sigma E_{\text{coh}}/V)^{1/2}$$

The monofunctional monomer (a) may be a mixture of monofunctional monomers. Given that such a monomer mixture contains n mols of a monomer (a1) with a solubility parameter value of SP_1 and m mols of a monomer (a2) with a solubility parameter value of SP_2 , then the solubility parameter value of the monomer mixture ($SP_{(\text{monomer})\text{mix}}$) is determined by the following equation, which is equally applied to determine the solubility parameter for monomer mixtures containing three or more monofunctional monomers:

$$SP_{(\text{monomer})\text{mix}} = (SP_1 \times n + SP_2 \times m) / (n + m).$$

Specific examples of such monofunctional monomers (a) include imide acrylate ($SP = 27.6$), N-vinyl-2-pyrrolidone ($SP = 26.2$), acryloyl morpholine ($SP = 25$), benzyl acrylate ($SP = 22.9$), phenoxyethyl acrylate ($SP = 22.6$), N,N-diethylacrylamide ($SP = 20.6$),

methoxypolyethylene glycol acrylate (ethylene oxide-added mol number $(n) = 9$, $SP = 19.6$),
methoxypolyethylene glycol acrylate (ethylene oxide-added mol number $(n) = 3$, $SP = 20.1$),
5 tetrahydrofurfuryl acrylate ($SP = 23$), and
phenoxypolyethylene glycol acrylate (ethylene oxide-added mol number $(n) = 6$, $SP = 20.7$). Of these,
benzyl acrylate, N-vinyl-2-pyrrolidone,
tetrahydrofurfuryl acrylate, and acryloyl morpholine
10 are preferred because of the high absorbability of the
film for the electrolyte solution. These monomers may
be used in combination of two or more. For the
purpose of optimizing the balance between the
absorbability of the film for the electrolyte solution
15 and the hardness of the film, it is particularly
preferred to use benzyl acrylate in conjunction with
acryloyl morpholine. In such a case, the ratio of
benzyl acrylate to acryloyl morpholine (by weight) is
preferably from 30/70 to 70/30. Acryloyl morpholine,
20 when present in excess, improves the absorbability of
the film for the electrolyte solution but makes the
film hard and susceptible to cracking.

The solubility parameter value of the nonaqueous
solvent is preferably in the range of 17 to 28 and,
25 more preferably, in the range of 18 to 23. If the
nonaqueous solvent has a solubility parameter value

that falls outside the specified range, then the solvent, when used in a lithium battery, can cause a decrease in the cycle performance of the battery.

Among the nonaqueous solvents for use in the present invention are carbonates, including dimethyl carbonate (SP = 17.4), propylene carbonate (SP = 20.8), and ethylene carbonate (SP = 22.5). These carbonates may be used either individually or in combination of two or more. One particularly preferred nonaqueous solvent is a mixed solvent ($SP_{(\text{solvent})\text{mix}} = 20.2$) containing equal volumes of dimethyl carbonate, propylene carbonate, and ethylene carbonate. Using the solubility parameter and the amount (in the number of mols) of each of the nonaqueous solvents used in the mixture, the solubility parameter of the mixed nonaqueous solvent can be determined in the same manner as in the determination of the solubility parameter of multiple monofunctional monomers used in combination.

The homopolymer of the monofunctional monomer (a) is preferably obtained by adding 0.1 to 5 parts by weight of a UV polymerization initiator (e.g., 2-hydroxy-2-methyl-1-phenylpropane-1-one, bis-acyl phosphine oxide, benzophenone, and 2-methylthioxanthone) to 100 parts by weight of the monofunctional monomer (a), and irradiating the

• mixture with UV rays with a wavelength of 250 to 350 nm at an energy density of 100 to 2000 mJ/cm² to polymerize the monomer.

According to the present invention, the
5 monofunctional monomer component (A) preferably contains the monofunctional monomer (a) in an amount of at least 20mol%. If too little of the monomer (a) is present, the amount of the nonaqueous solvent that can be absorbed by the liquid absorbing sheet may be
10 reduced.

As long as the advantages of the present invention are not affected, other monofunctional monomers, such as hydroxyethyl acrylate (SP = 29.6), acrylic acid (SP = 28.7), 2-ethylhexyl acrylate (SP =
15 18.9), and lauryl acrylate (SP = 18.7), may be added to the monofunctional monomer component (A).

The polyfunctional monomer component (B) for use in the present invention serves to introduce crosslinks in the liquid absorbing resin layer 1 and
20 is preferably a monomer having two or more acrylate residues. Examples of such monomers are hydroxyl pivalic acid neopentyl glycol diacrylate, polyethylene glycol diacrylate (ethylene oxide-added mol number (n) = 14), bisphenol A diacrylate, phenyl glycidyl ether
25 acrylate, and hexamethylene diisocyanate urethane prepolymer.

The amount of the polyfunctional monomer component (B) added to the monomer composition is such that the crosslink density preferably falls in the range of 0.0001 to 0.17 and, more preferably, in the range of 0.001 to 0.1. Too small an amount of the polyfunctional monomer component (B) may make it difficult for the liquid absorbing resin layer 1 to retain its shape, whereas too large an amount of the polyfunctional monomer component (B) may lead to an insufficient ability of the liquid absorbing resin layer 1 to absorb the nonaqueous solvent.

Given that 'a' indicates the number of the functional groups borne by a single molecule of the polyfunctional monomer, 'b' indicates the number of mols of the polyfunctional monomer present in the monomer composition, and 'c' indicates the number of mols of the monofunctional monomer present in the monomer composition, the crosslink density can be defined by the following equation:

$$\text{Crosslink density} = a \times b / (b + c).$$

The first configuration of the liquid absorbing sheet of the present invention as depicted in Fig. 1A can be obtained by coating a peelable film, such as polyethylene terephthalate film, with the above-

described monomer composition containing the monofunctional monomer component (A) and the polyfunctional monomer component (B), irradiating the coated film with UV rays to polymerize the composition and thereby form a sheet, and peeling the sheet from the peelable film. The second configuration as depicted in Fig. 1B can be obtained either by coating a nonwoven fabric with the monomer composition and polymerizing the composition, or by laminating a nonwoven fabric onto the first construction of Fig. 1A. The third construction as depicted in Fig. 1C can be obtained by further applying or laminating an adhesive over the liquid absorbing resin layer of the second configuration of Fig. 1B.

By using a peelable sheet embossed with surface patterns, the surface area of the liquid absorbing resin layer can be increased, resulting in an increase in the absorption rate of the liquid absorbing sheet.

The monomer composition containing the monofunctional monomer component (A) and the polyfunctional monomer component (B) may be directly applied to the inner surface of a battery case 21 as shown in Fig. 2, rather than onto the peelable film, such as polyethylene terephthalate film. Then, by irradiating with UV rays, the composition can be polymerized to form a sheet where it has been applied.

The monomer composition can be applied to the peelable sheet or nonwoven fabric by any suitable conventional technique, such as roll coater technique. The UV polymerization is typically carried out at 15 to 25°C while irradiating UV rays with a wavelength of 250 to 350 nm at an energy density of 100 to 2000 mJ/cm².

When the liquid absorbing resin layer itself shows adhesion (e.g., when the monofunctional monomer used in the component (A) is tetrahydrofurfuryl acrylate (SP = 23), benzyl acrylate (SP = 22.9), phenoxyethyl acrylate (SP = 22.6), phenoxypolyethylene glycol acrylate (ethylene oxide-added mol number (n) = 6, SP = 20.7), or methoxypolyethylene glycol acrylate (ethylene oxide-added mol number (n) = 3, SP = 20.1)), the construction of Fig. 1A or Fig. 1B can be directly attached to the battery pack without providing the adhesive layer. In addition, the liquid absorbing resin layer can be attached to the substrate by using a hand roller at room temperature, rather than by thermal lamination (See, Fig. 1B). Considering the fact that the leakage in many cases occurs at the cathode of the cylindrical batteries, the liquid absorbing sheet is preferably shaped as a doughnut-like shape in its plan view so that it can be applied about the cathode terminal.

According to the present invention, a flame retardant (e.g., phosphate-based liquid flame retardant, aluminum hydroxide, and melamine cyanurate) may be further added to the liquid absorbing resin layer 1 in the liquid absorbing sheet of the present invention. This imparts a flame retardancy to the liquid absorbing sheet. Specifically, when a phosphate-based liquid flame retardant is used as the flame retardant of the present invention, it can impart to the liquid absorbing resin layer 1 a flame retardancy of grade V-0, V-1, or V-2 according to the UL-94 standard. Furthermore, the phosphate-based flame retardant can impart a high adhesion to the liquid absorbing resin layer 1 since the agent remains a liquid under atmospheric pressure, typically at -13°C to 250°C, and preferably at room temperature. The liquid absorbing resin layer 1 that shows adhesion can be directly attached to the nonaqueous electrolyte secondary battery pack and, thus, can eliminate the need to provide an additional adhesive layer, so that the thickness of the liquid absorbing resin layer 1 does not have to be reduced by an amount corresponding to the thickness of the adhesive layer. Accordingly, the amount of the nonaqueous solvent that can be absorbed by the liquid absorbing sheet can be maintained. Moreover, we have unexpectedly found that

when the phosphate-based liquid flame retardant is used as the flame retardant of the present invention, the insulation resistance of the liquid absorbing resin layer 1 can be preferably maintained above $1 \times 10^{12} \Omega$ even after the liquid absorbing sheet has been subjected to a wet heat aging process (e.g., place the liquid absorbing sheet at a temperature of 40°C under a humidity of 90%RH for 96 hours).

Preferred examples of the phosphate-based liquid flame retardant for use in the present invention include bisphenol A bis(diphenyl)phosphate, hydroquinol bis(diphenyl)phosphate, phenyl dixylenyl phosphate, tricresyl phosphate, cresyl diphenyl phosphate, trixylenyl phosphate, xylenyl diphenyl phosphate, resorcinol bis(diphenyl)phosphate, and 2-ethylhexyl diphenyl phosphate. Of these, bisphenol A bis(diphenyl)phosphate, hydroquinol bis(diphenyl)phosphate and phenyl dixylenyl phosphate are preferred since they can impart high adhesion to the liquid absorbing resin layer 1.

The amount of the phosphate-based liquid flame retardant is preferably in the range of 70 to 200 parts by weight and, more preferably, in the range of 100 to 150 parts by weight with respect to 100 parts by weight of the monofunctional monomer component (A) and the polyfunctional monomer component (B) combined.

If too little or too much of the flame retardant is added, desired flame retardancy cannot be achieved.

The liquid absorbing sheet of the present invention is suitable as an electrolyte-absorbing
5 element used in a nonaqueous electrolyte battery pack that consists of a battery case encasing nonaqueous electrolyte battery cells, a circuit board, and the electrolyte-absorbing element. The liquid absorbing sheet serves to absorb the electrolyte solution should
10 leakage occur from the battery cell. One example of such a battery pack is shown in Fig. 2. The battery pack includes a battery case 21, which encases a circuit board 22 and a plurality of nonaqueous electrolyte battery cells 23 arranged on the circuit
15 board 22. A liquid absorbing sheet 26 as described above with reference to Fig. 1A is arranged between the circuit board 22 and the nonaqueous electrolyte battery cells 23 for absorbing the electrolyte solution should leakage occur from any of the
20 nonaqueous electrolyte battery cells. A metal lead 24 connects the circuit board 22 with each of the nonaqueous electrolyte battery cells 23. The metal lead 24 is also connected to external terminals 25. As shown in Fig. 3, a liquid absorbing sheet 27 as
25 described above with reference to Fig. 1C may be arranged on top of the nonaqueous electrolyte battery

cells 23 with its substrate facing the nonaqueous electrolyte battery cells 23.

Although the battery cases of the respective nonaqueous electrolyte battery packs shown in Figs. 2 and 3 are rectangular parallelepiped with cylindrical battery cells, the shape and arrangement of the battery case and the battery cells, as well as the type of the battery cells, are not limited to those shown in the figures and may vary depending on the intended purposes of the batteries.

As set forth, the nonaqueous electrolyte battery packs of the present invention include the liquid absorbing sheet, which serves as an element for absorbing electrolyte solution should leakage of the solution occur from the battery cells. The liquid absorbing sheet achieves this function by having a liquid absorbing resin layer that can effectively absorb and retain the nonaqueous electrolyte solution. This liquid absorbing resin layer is formed of a monomer composition that contains a monofunctional monomer component (A), which comprises a monofunctional monomer (a) capable of forming a homopolymer soluble in nonaqueous solvents used in nonaqueous electrolyte secondary batteries, and a polyfunctional monomer component (B). The liquid absorbing sheet, when used in nonaqueous electrolyte

battery packs, significantly reduces the occurrence of corrosion and short circuits of the circuit board in the event of leakage of the nonaqueous electrolyte solution.

5

Examples

The present invention will now be described in detail with reference to examples.

10 Reference Example

Homopolymers formed of different monofunctional monomers were examined for their solubility in a nonaqueous solvent used in nonaqueous electrolyte secondary batteries.

15 Specifically, 1 part by weight of a photopolymerization initiator (2-hydroxy-2-methyl-1-phenylpropane-1-one (D1173, Ciba Specialty Chemicals)) was added to 100 parts by weight of a monofunctional monomer. Using a roll coater, the mixture was applied
20 to a polyethylene terephthalate film and was irradiated with a UV-ray with a wavelength of 365 nm. The UV-ray was shone at an energy density of 2000 mJ/cm². This caused the composition to polymerize and thereby form a polymer film. 1 part by weight of the
25 resulting film was immersed in 300 parts by weight of a mixture containing equal volumes of

dimethylcarbonate, propylene carbonate, and ethylene carbonate ($SP_{(\text{solvent})\text{mix}} = 20.2$) at 23°C for 24 hours. Subsequently, the mixture was filtrated and the solid product remaining on the filter was dried at 100°C for 1 hour. The solubility (wt%) of the dried product was determined by the equation below with the results shown in Table 1. In the following equation, W_1 indicates the weight of the film prior to the immersion period and W_2 indicates the weight of the dried solid product:

$$\text{Solubility} = ((W_1 - W_2) / W_1) \times 100.$$

(Table 1)

Monofunctional monomer	SP value	ΔSP	Solubility (wt%)
Hydroxyethyl acrylate	29.6	9.4	3
Acrylic acid	28.7	8.5	5
Imide acrylate	27.6	7.4	100
N-vinyl-2-pyrrolidone	26.2	6.0	100
Acryloyl morpholine	25	4.8	100
Benzyl acrylate	22.9	2.7	100
Phenoxyethyl acrylate	22.6	2.4	85
N,N-diethylacrylamide	20.6	0.4	100
Methoxypolyethylene glycol acrylate (n=9)	19.6	-0.6	100
Methoxypolyethylene glycol acrylate (n=3)	20.1	-0.1	100
Phenoxypolyethylene glycol acrylate (n=6)	20.7	0.5	100
Tetrahydrofurfuryl acrylate	23.0	2.8	100
2-ethylhexyl acrylate	18.9	1.3	3

Examples 1 through 6 and Comparative Examples 1 through 3

One of the different monofunctional monomers shown in Tables 2 and 3, hydroxyl pivalic acid
5 neopentyl glycol diacrylate to serve as a polyfunctional monomer and 2-hydroxy-2-methyl-1-phenylpropane-1-one to serve as a polymerization initiator were mixed together in the proportions shown in Tables 2 and 3. Using a roll coater, the mixture
10 was applied to a polyethylene terephthalate film and was irradiated with a UV-ray with a wavelength of 365 nm. The UV-ray was shone at an energy density of 2000 mJ/cm² to cause the composition to polymerize and thereby form a polymer film. The polymer film was
15 peeled off from the polyethylene terephthalate film to give a single-layered liquid absorbing sheet.

The resulting liquid absorbing sheet was immersed in a large volume of a mixed solvent containing equal volumes of dimethylcarbonate, propylene carbonate, and
20 ethylene carbonate ($SP_{(\text{solvent})\text{mix}} = 20.2$) at 23°C. After 2 hours, the appearance of the liquid absorbing resin layer was visually examined. The liquid absorbing sheet was pulled out of the mixed solvent and the solvent remaining on the surface was immediately wiped
25 off. The sheet was weighed and its swell ratio was determined. The results are shown in Table 2. Each

liquid absorbing sheet was also examined for the SP value of the monofunctional monomer ($SP_{(\text{monomer})}$), the difference in the SP value between the monofunctional monomer and the solvent (ΔSP value), the density of crosslinks in the liquid absorbing resin layer of the liquid absorbing sheet and the state after the immersion period. The results are also shown in Tables 2 and 3.

10

(Table 2)

Components	Examples (wt parts)					
	1	2	3	4	5	6
Benzyl acrylate	100	100	100	—	30	100
N-vinyl-2-pyrrolidone	—	—	—	100	—	—
Acrylic acid	—	—	—	—	70	—
Polyfunctional monomer	1	0.1	10	1	1	20
Photopolymerization initiator	1	1	1	1	1	1
$SP_{(\text{monomer})}$	22.9	22.9	22.9	26.2	27.8	22.9
ΔSP	2.7	2.7	2.7	6.0	7.6	2.7
Crosslink density	0.010	0.001	0.091	0.007	0.005	0.167
Swell ratio (times)	10	10	3	10	3	1.6
State after immersion	Film	Gel	Film	Film	Film	Film

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(Table 3)

	Comparative Example (wt parts)		
	1	2	3
Benzyl acrylate	100	—	—
Acrylic acid	—	100	—
2-ethylhexyl acrylate	—	—	100
Polyfunctional monomer	—	1	1
Photopolymerization initiator	1	1	1
SP _(monomer)	22.9	28.7	18.9
Δ SP	2.7	8.5	-1.3
Crosslink density	0.000	0.005	0.005
Swell ratio (times)	Dissolved	1.1	1.1
State after immersion	Liquid	Film	Film

As shown by the results of Tables 2 and 3, the liquid absorbing sheet of Example 1 swelled 10 times and still retained its film-like shape after it had swollen by absorbing the nonaqueous solvent. This implies that this liquid absorbing sheet can serve as an effective liquid absorbing element for absorbing the electrolyte solution should leakage of the solution occur from the nonaqueous electrolyte battery cells.

The results also indicate that the liquid absorbing sheets of Examples 2 through 6 each exhibits a good performance that allows the practical use of the liquid absorbing sheet as an element for absorbing the electrolyte solution. Nonetheless, the results of Example 2 indicate that the liquid absorbing sheet with a decreased crosslink density tends to become a

gel-like material, rather than retaining its film-shape, after absorbing the nonaqueous solvent and swelling. In contrast, the results of Examples 3 and 6 show that an increased crosslink density tends to result in a decreased swell ratio. The results of Example 4 indicate that a good result can be achieved by using, rather than benzyl acrylate, N-vinyl-2-pyrrolidone as the monofunctional monomer. The results of Example 5 indicate that when a monofunctional monomer whose homopolymer is insoluble in the nonaqueous solvent is used together, the swell ratio of the liquid absorbing sheet tends to decrease.

On the other hand, the results of Comparative Example 1 indicate that the polyfunctional monomer-free liquid absorbing resin layer dissolves in the nonaqueous solvent and thus cannot be used as the element for absorbing the electrolyte solution. The results of Comparative Example 2 indicate that when the monofunctional monomer has too large a SP value so that its homopolymer is substantially insoluble in the nonaqueous solvent, the swell ratio of the liquid absorbing sheet becomes too small, making the liquid absorbing sheet unsuitable for use as the element for absorbing the electrolyte solution. The results of Comparative Example 3 indicate that when the monofunctional monomer has too small a SP value so

that its homopolymer is again substantially insoluble in the nonaqueous solvent, the swell ratio of the liquid absorbing sheet becomes too small, making the liquid absorbing sheet unsuitable for use as the
5 element for absorbing the electrolyte solution.

Example 7 (Test for the ability to absorb an electrolyte solution using a simulated battery pack)

As shown in Fig. 4, a 7.0 cm (l) × 7.9 cm (w) ×
10 2.3 cm (h) ABS resin box 41 was obtained. A 6.5 cm (l) × 6.5 cm (w) 100 μm-thick liquid absorbing sheet 42 prepared according to Example 1 was stuck to the bottom of the box with a commercially available adhesive. Three lithium ion batteries 43 were placed
15 on the liquid absorbing sheet 42, and a glass epoxy substrate 44 as a circuit board was placed adjacent to the batteries.

A hole h was drilled through the side wall of one of the batteries 43 that was in the middle of the
20 three. The electrolyte solution leaking from the hole was allowed to be absorbed by the liquid absorbing sheet. After drilling of the hole h, the batteries were left for one day and night and the inside of the battery pack was observed. It turned out that the
25 glass epoxy substrate was not wet. In addition, the decrease in weight of the battery with the hole h

drilled in it was 2.5 g, which was equal to the increase in weight of the liquid absorbing sheet. These observations suggest that the leaked electrolyte solution was entirely absorbed by the liquid absorbing sheet.

Examples 8 through 15

One of the different monofunctional monomers shown in Table 4, polyethylene glycol diacrylate to serve as a polyfunctional monomer (ethylene glycol-added mol number = 14, 14EG-A, Kyoeisha Chemical) and 2-hydroxy-2-methyl-1-phenylpropane-1-one to serve as a polymerization initiator were mixed together in the proportions shown in Table 4. Using a roll coater, the mixture was applied to a polyethylene terephthalate film and was irradiated with a UV-ray with a wavelength of 365 nm. The UV-ray was shone at an energy density of 2000 mJ/cm² to cause the composition to polymerize and thereby form a polymer film. The polymer film was then peeled off from the polyethylene terephthalate film to give a single-layered liquid absorbing sheet (210 g/m²).

Meanwhile, an electrolyte solution was prepared by adding lithium phosphate hexafluoride to serve as an electrolyte to a mixed solvent containing equal volumes of dimethylcarbonate, propylene carbonate, and

ethylene carbonate ($SP_{(\text{solvent})\text{mix}} = 20.2$). 0.2ml of this electrolyte solution was added dropwise onto 0.03g of the liquid absorbing sheet and the time it took for the solution to be completely absorbed by the liquid
5 absorbing sheet was visually measured. The liquid absorbing sheet was also immersed in a large volume of the electrolyte solution at 23°C. After 3 hours, the appearance of the liquid absorbing resin layer was visually examined. The liquid absorbing sheet was
10 pulled out of the mixed solvent and the solvent remaining on the surface was immediately wiped off. The sheet was weighed and its swell ratio was determined. Furthermore, the liquid absorbing sheet was heated in a wet heat oven (40°C, 90%RH, 96hrs) and
15 was examined for the degree of swelling. The results are shown in Table 5.

In addition, a 5cm wide strip of a polypropylene nonwoven fabric (Unitika) was laminated onto either side of the liquid absorbing sheet using the hand
20 roller technique (23°C) or the thermal lamination technique (80°C). The adhesion strength was then determined on a tensile tester (TENSILON, Orientech) used in T-peel mode. Also, a 3cm wide strip of the liquid absorbing sheet was laminated onto an Ni
25 surface using the hand roller technique (23°C) or the thermal lamination technique (80°C). The adhesion

strength was then determined on a tensile tester (TENSILON, Orientech) used in T-peel mode. The results are shown in Table 5.

Each liquid absorbing sheet was also examined for the SP value of the monofunctional monomer ($SP_{\text{(monomer)}}$), the difference in the SP value between the monofunctional monomer and the solvent (ΔSP value), the density of crosslinks in the liquid absorbing resin layer of the liquid absorbing sheet and the state after the immersion period. The results are also shown in Table 5.

(Table 4)

[illegible]

(Table 5)

Components	Examples							
	8	9	10	11	12	13	14	15
(Degree of swelling) W/O wet heat process								
Dropwise addition (min)	30	100	120	40	15	15	120<	180
Immersed (times)	9.0	9.4	9.6	8.2	8.6	9.0	2.3	18
(Degree of swelling) With wet heat process								
Dropwise addition (min)	30	130	160	60	20	25	120<	200
Immersed (times)	9.0	9.2	9.0	8.1	8.5	8.5	2.0	17
Adhesion strength to nonwoven fabric								
Hand roller (kg/5cm)	0.4	0.03	0.03	0.1	0.03	0	0	0
Thermal lamination (kg/5cm)	0.7	0.03	0.03	0.1	0.03	0	0	0.3
Adhesion strength to Ni surface								
Hand roller (kg/3cm)	0.3	0.02	0.02	0.08	0.03	0	0	0
SP _(monomer)	23	22.9	22.6	20.7	20.1	19.6	25	20.6
Δ SP	2.8	2.7	2.4	0.5	-0.1	-0.6	4.8	0.4
Crosslink density	0.002	0.002	0.003	0.004	0.003	0.006	0.002	0.002
State after immersion	Film	Film	Film	Film	Film	Film	Film	Film

As shown by the results of Table 5, the liquid absorbing sheets of Examples 8 through 13 each swelled approximately 8 to 9 times after the immersion period and still retained the film-like shape after they had swollen by absorbing the nonaqueous solvent. This implies that each of these liquid absorbing sheets, while exhibiting varying absorption rates upon dropwise addition of a predetermined amount of the nonaqueous solvent, can serve as an effective liquid

absorbing element for absorbing the electrolyte solution should leakage of the solution occur from the nonaqueous electrolyte battery cells.

Although the liquid absorbing sheet of Example 14
5 swelled at a less swell ratio than the liquid absorbing sheets of Examples 8 through 13, the sheet exhibited a good performance that would allow the practical use of the liquid absorbing sheet as an element for absorbing the electrolyte solution.

10 While the liquid absorbing sheet of Example 15 showed a slower absorption rate than the liquid absorbing sheets of Examples 8 through 13, it had a good swell ratio.

The liquid absorbing sheets of Examples 8 through
15 12 each had an liquid absorbing resin layer that itself showed adhesion, so that they did not require a separate adhesion layer. In particular, the liquid absorbing resin layer of the liquid absorbing sheet of Example 8 showed superior adhesion.

20 Example 16 (Experiments a through e), Comparative Example 4 (Experiments f through h), and Comparative Example 5

The following components were mixed together in
25 the proportions shown in Tables 1 and 2: one of the different monofunctional monomers shown in Tables 6

and 7, urethane acrylate (AH600, Kyoeisha) to serve as a polyfunctional monomer, 2-hydroxy-2-methyl-1-phenylpropane-1-one (D1173, Ciba Specialty Chemicals) to serve as a polymerization initiator and a
5 phosphate-based liquid flame retardant or an ammonium polyphosphate-based solid flame retardant. Using a roll coater, the mixture was applied to a polyethylene terephthalate film and was irradiated with a UV-ray with a wavelength of 365 nm. The UV-ray was shone at
10 an energy density of 2000 mJ/cm² to cause the composition to polymerize and thereby form a polymer film. A flame-retardant nonwoven fabric (Japan Vilene) was then laminated over the polymer film and the polyethylene terephthalate film was removed to
15 obtain a double-layered liquid absorbing sheet.

Each of the liquid absorbing sheets so obtained was tested for the flame retardancy, adhesion, swell ratio upon absorption of the electrolyte solution and insulating performance. The tests were conducted in
20 the following manner.

<Flame retardancy>

The flame retardancy of each liquid absorbing sheet was evaluated according to the UL-94 standard.
25 The results are shown in Tables 6 and 7. The flame retardancy of grade V-0, V-1, or V-2 indicates that

the absorbance sheet has sufficient flame retardancy for practical use.

<Adhesion>

5 A 5cm wide strip of a polypropylene nonwoven fabric (Japan Vilene) was laminated onto the liquid absorbing sheet over the liquid absorbing resin layer using the hand roller technique (23°C). The adhesion strength was then determined on a tensile tester
10 (TENSILON, Orientech) used in T-peel mode. The results are shown in Tables 6 and 7.

<Swell Ratio>

 An electrolyte solution was prepared by adding
15 lithium phosphate hexafluoride to serve as an electrolyte to a mixed solvent containing equal volumes of dimethylcarbonate, propylene carbonate and ethylene carbonate. The lithium phosphate hexafluoride was added to a concentration of 1mol/l.
20 The liquid absorbing sheet was immersed in the electrolyte solution at 23°C. After 3 hours, the liquid absorbing sheet was pulled out of the solution and the solution remaining on the surface was immediately wiped off. The sheet was weighed and its
25 swell ratio was determined. The results are shown in Tables 6 and 7.

<Insulating performance>

The insulation resistance (Ω) of the liquid absorbing resin layer of each liquid absorbing sheet was determined before and after the wet heat process.

5 The results are shown in Tables 6 and 7.

(Table 6)

Components	Example 16 (Wt parts)				
	Experiment a	Experiment b	Experiment c	Experiment d	Experiment e
Benzyl acrylate	70	70	70	70	70
Acryloyl morpholine	30	30	30	30	30
Polyfunctional monomer	0.5	0.5	0.5	0.5	0.5
Photopolymerization initiator	0.5	0.5	0.5	0.5	0.5
Bisphenol A bis(diphenyl)phosphate	70	100	150	200	-
Hydroquinol bis(diphenyl)phosphate	-	-	-	-	100
Flame retardancy(UL-94)	V-0	V-0	V-0	V-2	V-2
Adhesion (kgf/5cm)	0.4	0.6	0.5	0.5	0.7
Swell Ratio (Times)	9	8	6	6	7
Insulating performance (Ω) (before wet heat process)	4×10^{12}	4×10^{12}	3×10^{12}	3×10^{12}	1×10^{10}
Insulating performance (Ω) (after wet heat process)	1×10^{12}	1×10^{12}	1×10^{12}	1×10^{12}	1×10^9

(Table 7)

Components	Comparative Example 4 (wt parts)			Comparative Example 5 (wt parts)
	Experi- ment f	Experi- ment g	Experi- ment h	
Benzyl acrylate	70	70	70	70
Acryloyl morpholine	30	30	30	30
Polyfunctional monomer	0.5	0.5	0.5	0.5
Photopolymerization initiator	0.5	0.5	0.5	0.5
Bisphenol A bis(diphenyl)phosphate	0	50	250	-
Ammonium polyphosphate	-	-	-	200
Flame retardancy (UL-94)	NA	NA	NA	V-0
Adhesion (kgf/5cm)	NA	NA	0.3	NA
Swell Ratio (Times)	9	9	4	-
Insulating performance (Ω) (before wet heat process)	9×10^{13}	9×10^{13}	9×10^{13}	3×10^{14}
Insulating performance (Ω) (after wet heat process)	2×10^{12}	2×10^{12}	2×10^{12}	3×10^{10}

As shown by the results of Table 6, the liquid absorbing sheets of Experiments a through d of Example 16 each had a good flame retardancy and adhesion, swelled 6 times or more, and exhibited a superior insulating performance. The liquid absorbing sheet of Experiment e had a high flame retardancy, adhesion, and swell ratio comparable to those of the liquid absorbing sheets of Experiments a through d. In fact,

the liquid absorbing sheet of Experiment e showed higher adhesion than the other liquid absorbing sheets. While the liquid absorbing sheet of Experiment e had relatively low insulating performance, the fluctuation of the insulating performance was small over the wet heat process, proving high storage stability of the liquid absorbing sheet.

The results of Table 7 for the liquid absorbing sheets of Experiments f through h of Comparative Example 4 indicate that the desired flame retardancy may not be achieved not only when bisphenol A bis(diphenyl)phosphate, a phosphate-based liquid flame retardant, is not added, but also when its amount is too little or too much. The liquid absorbing sheet of Comparative Example 5, which used the ammonium polyphosphate-based solid flame retardant, showed no adhesion, and its insulation performance was significantly decreased after the wet heat process.

Example 17 (Test for the ability to absorb an electrolyte solution using a simulated battery pack)

As shown in Fig. 4, a 7.0cm (l) × 7.9 cm (w) × 2.3 cm (h) ABS resin box 41 was obtained. A 6.5cm (l) × 6.5 cm (w) 100 μm-thick liquid absorbing sheet 42 prepared according to Example 1 was stuck to the bottom of the box with a commercially available

adhesive. Three lithium ion batteries 43 were placed on the liquid absorbing sheet 42, and a glass epoxy substrate 44 as a circuit board was placed adjacent to the batteries.

5 A hole h was drilled through the side wall of one of the batteries 43 that was in the middle of the three. The electrolyte solution leaking from the hole was allowed to be absorbed by the liquid absorbing sheet. After drilling of the hole h, the batteries
10 were left for one day and night and the inside of the battery pack was observed. It turned out that the glass epoxy substrate 44 was not wet. In addition, the decrease in weight of the battery with the hole h drilled in it was 2.5g, which was equal to the
15 increase in weight of the liquid absorbing sheet. These observations suggest that the leaked electrolyte solution was entirely absorbed by the liquid absorbing sheet.

20 INDUSTRIAL APPLICABILITY

As set forth, the liquid absorbing sheet of the present invention includes a liquid absorbing resin layer that can effectively absorb the nonaqueous electrolyte solution used in nonaqueous electrolyte
25 secondary batteries. This makes the liquid absorbing sheet an effective liquid-absorbing element suitable

for use in nonaqueous electrolyte battery packs (in particular, in lithium ion-based nonaqueous electrolyte secondary battery packs).

5 A phosphate-based liquid flame retardant may be added to the liquid absorbing resin layer of the liquid absorbing sheet of the present invention. When added, the agent imparts superior flame retardancy to the liquid absorbing sheet. As a result, not only does the liquid absorbing sheet exhibit the high
10 ability to absorb the nonaqueous electrolyte solution, which is required in nonaqueous electrolyte secondary batteries to make nonaqueous electrolyte battery packs (in particular, in lithium ion-based nonaqueous electrolyte secondary battery packs), but it also
15 shows adhesion and superb flame retardancy. Accordingly, the liquid absorbing sheet of the present invention is suitable as a liquid-absorbing element for absorbing the electrolyte solution in nonaqueous electrolyte battery packs.